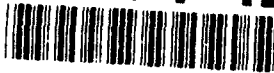


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## 13. ABSTRACT (Maximum 200 words)

Electrical and optical measurements of ZnS:Mn alternating-current thin-film electroluminescent (ACTFEL) devices grown by atomic layer epitaxy provide evidence for the existence of space charge within the bulk ZnS layer. Blue luminescence is observed during the falling edge of an applied voltage pulse when the ACTFEL device is operated at low temperature. This blue luminescence is attributed to donor-acceptor pair radiative recombination in which chlorine is identified as the donor and a zinc vacancy as the acceptor. This luminescence identification leads to determination of the origin of space charge as arising from impact ionization of the zinc vacancy.

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# Evidence for space charge in atomic layer epitaxy ZnS:Mn alternating-current thin-film electroluminescent devices

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Electrical and optical measurements of ZnS:Mn alternating-current thin-film electroluminescent (ACTFEL) devices grown by atomic layer epitaxy provide evidence for the existence of space charge within the bulk ZnS layer. Blue luminescence is observed during the falling edge of an applied voltage pulse when the ACTFEL device is operated at low temperature. This blue luminescence is attributed to donor-acceptor pair radiative recombination in which chlorine is identified as the donor and a zinc vacancy as the acceptor. This luminescence identification leads to determination of the origin of space charge as arising from impact ionization of the zinc vacancy.

## I. INTRODUCTION

In the device physics assessment of alternating-current thin-film electroluminescent (ACTFEL) devices, it is usually assumed<sup>1-4</sup> that the electric field is constant across the phosphor layer; this implies that no net space charge exists within the bulk portion of the phosphor layer. Although this assumption is almost universally employed, its validity has been questioned by numerous researchers.<sup>1-12</sup>

Most discussions of space charge in ACTFEL devices have focussed on explaining the mechanism responsible for hysteresis in brightness-voltage ( $B$ - $V$ ) curves.<sup>5-10</sup>  $B$ - $V$  hysteresis is found to occur in ACTFEL devices when the Mn concentration exceeds about 0.5%.<sup>7</sup> Models accounting for  $B$ - $V$  hysteresis invoke<sup>5-8</sup> the existence of positive space charge in the ZnS phosphor due to hole trapping or impact ionization of deep levels within the ZnS band gap. Although atomic identification of this positive space charge has never been clearly established, the existent evidence suggests<sup>6,7</sup> it to be related to Mn and probably due to Mn clustering.

Recently, evidence has been offered<sup>11,12</sup> for the existence of space charge in nonhysteretic, atomic layer epitaxy (ALE) ZnS:Mn ACTFEL devices. This conclusion is reached from scaling analysis of the conduction current with respect to frequency. The purpose of this article is to provide supporting evidence for the existence of bulk space charge in ALE-grown ZnS:Mn ACTFEL devices as deduced from electrical and optical measurements at low temperature.

## II. EXPERIMENTAL PROCEDURE

The ZnS:Mn ACTFEL devices measured in this work are fabricated by ALE in the typical stack configuration in

which the ZnS:Mn phosphor layer is sandwiched between layers of aluminum-titanium oxide (ATO) which are contacted by indium tin oxide (ITO) and aluminum electrodes. The ACTFEL device is driven using an arbitrary waveform generator (Analogic model 2020) in conjunction with a high voltage operational amplifier (Apex model PA85) to obtain alternating bipolar pulses with amplitudes of magnitude 160 V, rise/fall times of 80  $\mu$ s, pulse width of 160  $\mu$ s, and a frequency of 100 Hz. Electrical characterization is accomplished using a digitizing oscilloscope (Tektronix model 11402) to monitor the voltage across the ACTFEL device and a sense capacitor (Sawyer-Tower configuration). The current is monitored with a current probe (Tektronix model A6302 with an AM503 current probe amplifier).

Time-resolved luminescence spectra are measured using a SPEX 3/4 m monochromator and a cooled, extended range photomultiplier tube (PMT). Spectra are obtained by digitally acquiring the voltage across a resistor between the PMT and ground. A single-system correction to the raw data is performed which accounts for the lenses, grating, and detector.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

The voltage and current transients for an ACTFEL device at room temperature are given in Fig. 1(a). During the initial rising edge of the voltage pulse, the device behaves as a capacitive stack and all of the measured current is displacement current. Once the amplitude of the voltage becomes sufficiently large, electrons at the phosphor/insulator interface begin to emit and conduction current flows across the phosphor layer; we refer to this as primary conduction current. During the falling edge of the voltage

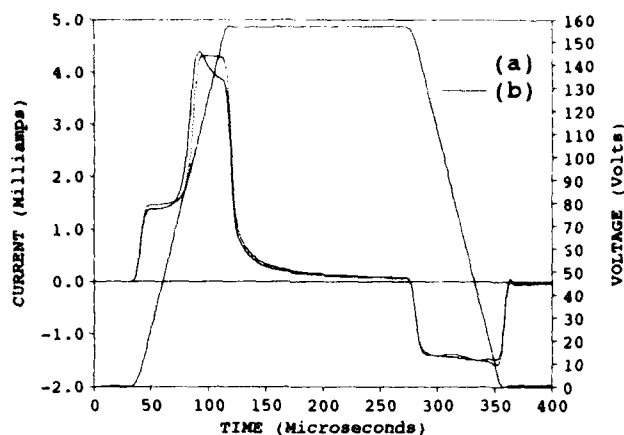


FIG. 1. Voltage and current transients for an ALE ZnS:Mn ACTFEL device operating at (a) room temperature and (b) approximately 50 K.

pulse the device appears as a capacitive stack once again and the measured current is exclusively displacement current.

As shown in Fig. 1(b) at low temperatures two small additional current peaks, subsequently referred to as comprising a secondary conduction current, are observed during the falling edge of the voltage pulse. Using a bridge circuit to balance out the displacement current below threshold, these secondary current peaks are confirmed to arise from conduction current which flows in an opposite direction to that of the primary current. These secondary current peaks are only found to occur during the falling edge of a negative pulse applied to the Al electrode. Additionally, with increasing temperature the magnitude of these secondary current peaks decreases and they shift in time closer to the initial transition of the voltage pulse, as shown in Fig. 2.

The appearance of secondary current, as manifest by these two current peaks, is correlated with changes in the shape of the primary conduction current. As shown in Fig. 3(a), the top portion of the conduction current is essentially flat at room temperature. In contrast at low temper-

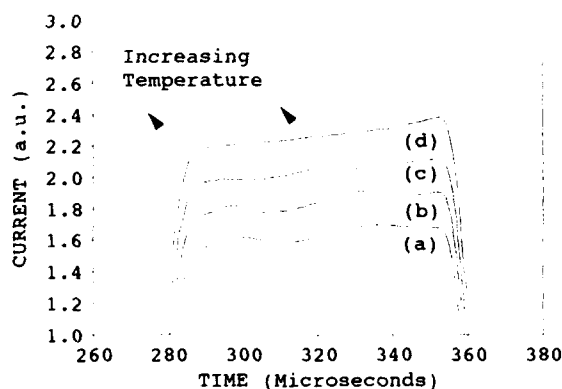


FIG. 2. Secondary conduction current peaks superimposed on the displacement current background of the falling edge of a voltage pulse for an ALE ZnS:Mn ACTFEL device at the following temperatures: (a) 50 K, (b) 100 K, (c) 150 K, and (d) 300 K.

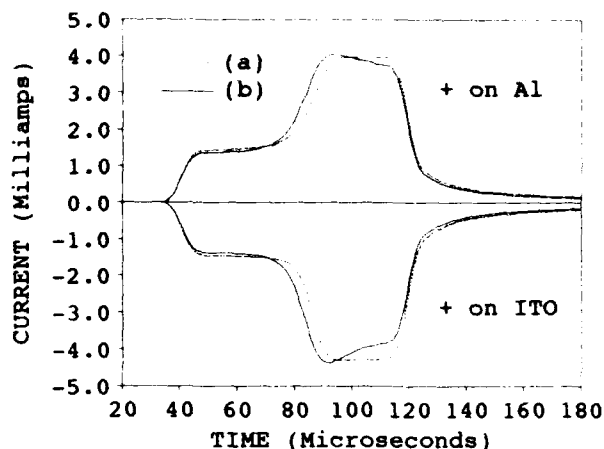


FIG. 3. Primary conduction current transient for an ALE ZnS:Mn ACTFEL device operating at (a) room temperature and (b) approximately 50 K.

ature, as indicated in Fig. 3(b), a new peak is superimposed upon the flat portion of the primary conduction current.

In order to further investigate the secondary current peaks, time-resolved luminescence measurements are performed. Figure 4 displays the luminescence and average phosphor electric field transients at a wavelength of 460 nm and a temperature of about 50 K. The first luminescence peak is concomitant with the flow of primary conduction current, while two additional luminescence features occur during the falling edge of the voltage waveform, when the secondary conduction current peaks are found. Note that the peak height of the first additional luminescence peak is larger than that of the primary peak but that the integrated intensity of the primary peak is larger. Also, notice that the first additional luminescence peak occurs before the phosphor electric field has reversed sign. In contrast, the second additional luminescence peak is weak and is initiated concomitant with a reversal of the phosphor field direction.

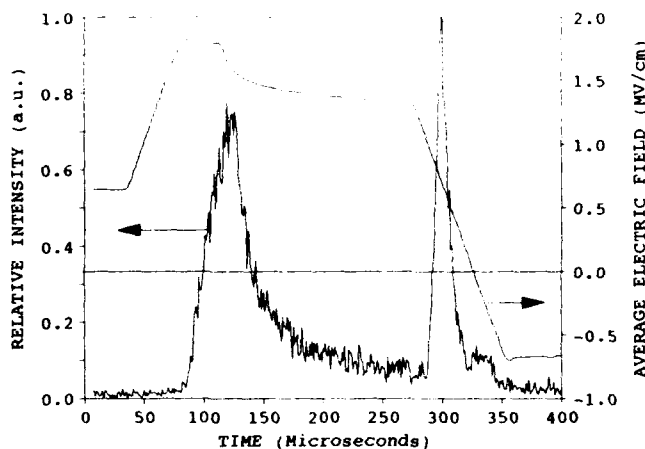


FIG. 4. Luminescence and average phosphor electric field transients for an ALE ZnS:Mn ACTFEL device at a wavelength of 460 nm and a temperature of approximately 50 K.

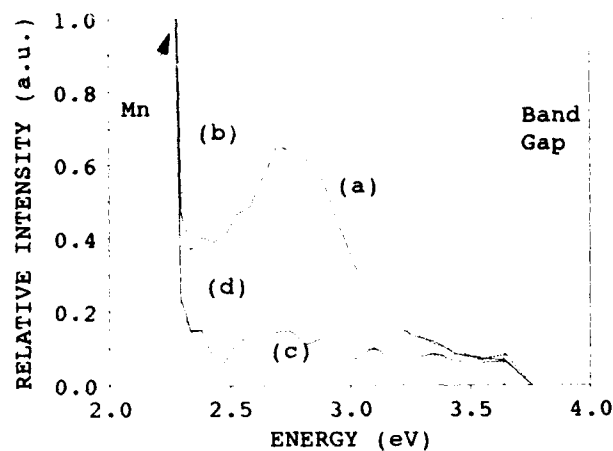


FIG. 5. Luminescence spectra for an ALE ZnS:Mn ACTFEL device at a temperature of approximately 50 K corresponding to the following conditions: (a) primary conduction current for a negative pulse to the ITO electrode, (b) primary conduction current for a negative pulse to the Al electrode, (c) secondary conduction current for a negative pulse to the ITO electrode, and (d) secondary conduction current for a negative pulse to the Al electrode.

The low temperature luminescence spectra corresponding to primary and secondary currents for both voltage polarities are given in Fig. 5. Note that the measured intensity of secondary luminescence is significant only when the Al electrode is negatively biased. Although there are differences in the spectra shown in Fig. 5, the similar shape and peak energy (approximately 2.7 eV or 460 nm which puts it in the blue region of the electromagnetic spectrum) of the spectra are striking. Thus we believe the primary and secondary blue luminescence associated with both voltage polarities can be attributed to the same physical process.

In summary, at low temperature we observe blue luminescence centered at approximately 460 nm and which occurs concomitant with the flow of either primary or secondary conduction current. Furthermore, this blue luminescence exhibits thermal quenching in which the intensity decreases with increasing temperature. These luminescence features are remarkably similar to photoluminescence (PL) spectra measured<sup>13</sup> by Mikami *et al.* from ZnS:Mn layers grown by halide-transport chemical vapor deposition. Specifically, Mikami *et al.* observed strong blue PL emission with a peak at 460 nm and which exhibited thermal quenching by a factor of 1/3 on raising the temperature from 77 to 300 K. Moreover, they did not see this blue luminescence unless HCl was used in the growth; our ALE phosphor contains some chlorine since it is grown using zinc chloride as a source gas. These striking similarities between our blue luminescence and the PL measured by Mikami *et al.* strongly suggests that they arise from the same physical process.

Various considerations led Mikami *et al.*<sup>13</sup> to identify this blue luminescence as due to radiative recombination from a shallow chlorine donor sitting on a sulfur site,  $\text{Cl}_\text{S}$ , to a deep acceptor, identified as a zinc vacancy,  $V_\text{Zn}$ . The ionization energy of  $\text{Cl}_\text{S}$  is reported<sup>14</sup> to be about 0.1–0.3

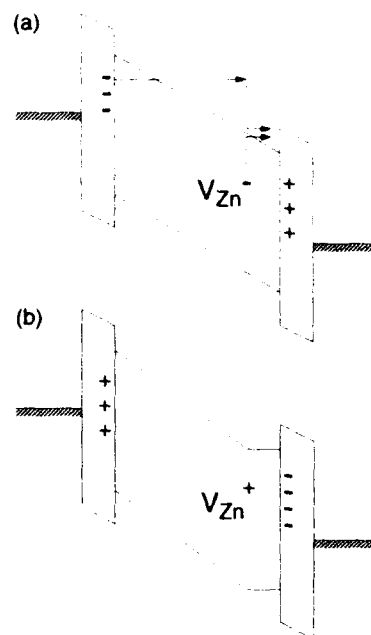


FIG. 6. Energy band diagrams illustrating a model for the origin of space charge in an ALE ZnS:Mn ACTFEL device at (a) the initiation of primary current flow in which an electron tunnels from the cathode interface, gains energy from the field, impact ionizes a  $V_\text{Zn}$  acceptor, and both are electrons trapped at the anode interface and (b) after the flow of conduction current when a low-field region is formed near the anode interface due to the existence of positive space charge.

eV which places the  $V_\text{Zn}$  level at about 1 eV above the ZnS valence band maximum,  $E_\text{V}$ . This level is probably due to the second acceptor state of the  $V_\text{Zn}$  which has been crudely estimated<sup>15</sup> to be located about 1.5 eV above  $E_\text{V}$ . Thus the blue luminescence we observe is attributed to donor-acceptor pair radiative recombination in which  $\text{Cl}_\text{S}$  is the donor and the second ionization state of  $V_\text{Zn}$  is the deep acceptor.

It should be recalled,<sup>2</sup> that donor-acceptor pair recombination is not an efficient luminescence mode for devices which operate under high field conditions. Perhaps this can be reconciled with the fact that our blue luminescence intensity is orders of magnitude weaker than that of Mn. We believe, however, that the intensity of the blue luminescence is sufficiently strong to require the existence of a low-field region within the ZnS.

Postulating the existence of such a low-field region leads to the following space charge model for an ALE ZnS:Mn ACTFEL device which is illustrated by Fig. 6. Figure 6(a) shows the energy band diagram at the initiation of the flow of conduction current. Negative charge due to electrons occupying interface states is indicated at the left interface while positive charge, associated with empty interface states, is shown at the right interface. An electron at the left interface is shown to tunnel from the interface, gain energy from the field, impact ionize a  $V_\text{Zn}$  deep level, and drift to the opposite interface with the ionized electron where both electrons are trapped at interface states. Impact ionization of  $V_\text{Zn}$ 's is hypothesized to occur near the opposite (anode) interface since the electrons have more oppor-

tunity to gain energy from the field and since it is more likely that  $V_{Zn}$ 's occur near the interface than in the bulk.

Figure 6(b) shows the energy band situation after conduction current is transferred but the external bias is maintained at a constant voltage. Charge transfer results in a reduction of the voltage across the phosphor and a corresponding increase in the voltage across the insulators. Impact ionization of  $V_{Zn}$ 's leads to the buildup of positive space charge since the ionization state goes from a double negative charge to a single negative. If a large amount of charge is generated by impact ionization and the charge centroid for this positive charge is centered close to the right interface (e.g., perhaps 100–500 Å), then the phosphor field near the right interface can be significantly reduced, as shown in Fig. 6(b). We believe that it is the formation of a low-field region near the anode interface which leads to the relatively high efficiency of the blue luminescence which we observe in ALE ZnS:Mn ACTFEL devices. The asymmetrical nature of the secondary blue luminescence shown in Fig. 5 suggests that the  $Cl_s$  and  $V_{Zn}$  concentrations are greater near the ITO interface.

It is likely that the relatively high intensity of the blue luminescence at low temperature arises at least partially from the fact that the efficiency of impact ionization increases at low temperature.<sup>16</sup> The reduced phonon density also contributes to the higher intensity of the blue luminescence at low temperature.

#### IV. CONCLUSIONS

Low temperature current and luminescence measurements provide evidence for the existence of space charge within the bulk ZnS:Mn phosphor of an ALE-grown ACTFEL device. Similarities between the luminescence observed in this work and PL measured by Mikami *et al.*<sup>13</sup> lead to an identification of this luminescence as arising

from donor-acceptor pair radiative recombination via a chlorine donor and a zinc vacancy. The implication of this identification is that ionization of the second acceptor level of the zinc vacancy by impact ionization leads to the formation of space charge in ALE ZnS:Mn ACTFEL devices.

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